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Improved Methods of Analysis for Chlorate, Chlorite, and Hypochlorite Ions at the Sub-mg/L Level

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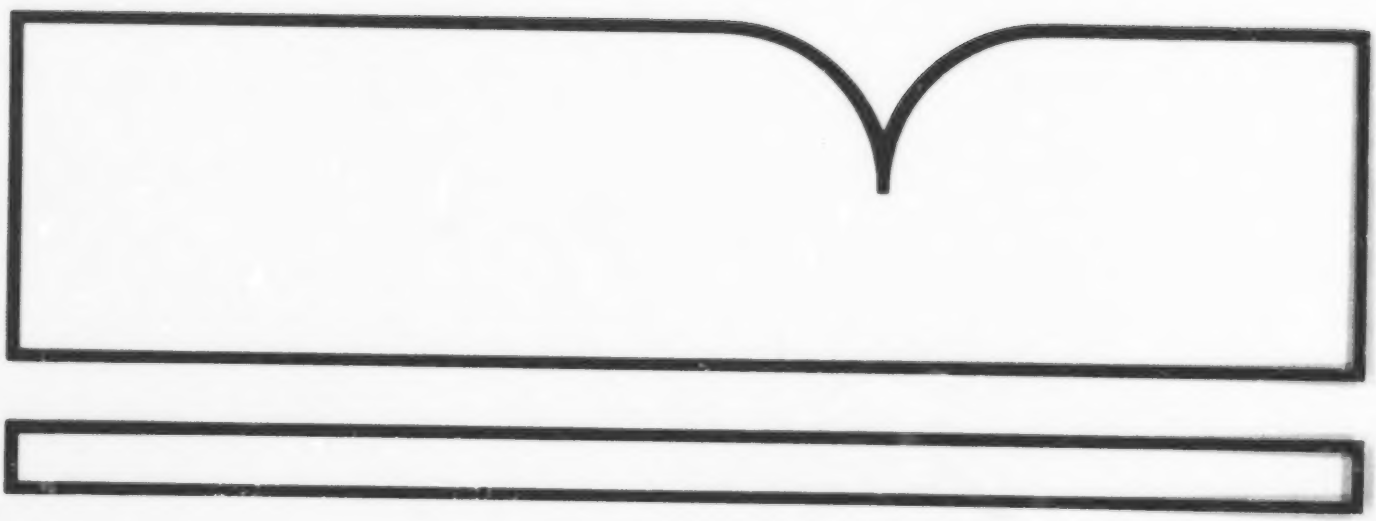

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IMPROVED METHODS OF ANALYSIS FOR CHLORATE, CHLORITE, AND HYPOCHLORITE IONS AT THE SUB-mg/L LEVEL

by

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A modified iodometric method is reported to measure chlorate ion at the sub-mg/L level with high precision and accuracy. Hexane and nitrogen are used as shielding agents. Chlorate ion is reduced by iodide ion in 6M hydrochloric acid. Saturated sodium phosphate solution is used to lower the hydrogen ion and the liberated iodine is titrated with standard sodium thiosulfate. The end-point is detected using Thyodene as the indicator or by the color of iodine in the hexane layer. A potentiometric end-point is recommended for the determination of chlorate ion at concentrations less than 1.0×10^{-4} N (3.5 mg/L). Chlorate ion at the sub-mg/L level can be determined with a precision of better than ±1% with a lower detection limit of 0.1 mg/L. An analytical scheme is reported to speciate hypochlorite, chlorite, and chlorate ions in a mixture at the sub-mg/L level. Chlorate ion is determined directly by a modified iodometric method. Chlorite ion is determined directly by the modified Suzuki-Gordon method where the chlorine and hypochlorous acid are converted to hypochlorite ion. The hypochlorite ion in the mixture is reduced to chloride ion by sulfite ion at pH 10.5 followed by oxidation of excess sulfite ion by iodine. Following this oxidation, chlorite ion is reduced to chloride ion by iodide at pH 2. Hypochlorite ion is determined indirectly from the results. The titration end-point is determined by a potentiometric method. The overall precision is ±3% for oxychlorine species at concentrations in the range of 0.3 - 100 mg/L with lower detection limits of 0.1 mg/L.

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FOREWORD

Environmental measurements are required to determine the quality of ambient waters and the character of waste effluents. The Environmental Monitoring and Support Laboratory (EMSL)-Cincinnati conducts research to:

- Develop and evaluate techniques to measure the presence and concentration of physical, chemical, radiological pollutants in water, wastewater, bottom sediments, and solid waste.
- Investigate methods for the concentration, recovery, and identification of viruses, bacteria, and other microorganisms in water.
- Conduct studies to determine the responses of aquatic organisms to water quality.
- Conduct an Agency-wide quality assurance program to assure standardization and quality control of systems for monitoring water and waste water.

This report describes the development of a sensitive and accurate method for the determination of chlorate, chlorite, and hypochlorite ions. Chlorate and chlorite ions are physiologically active; therefore, their concentration must be monitored in drinking water which has been treated with chlorine dioxide. Prior to the start of this project no existing analytical method was capable of precisely and accurately determining these ions at the low estimated acceptable levels.

Robert L. Booth, Director
Environmental Monitoring and
Support Laboratory - Cincinnati

ABSTRACT

A comparison is given of existing analytical methods of analysis for the oxyhalogen species including chlorate ion, chlorite ion, and hypochlorous acid/-chlorine. Known limitations of the methods and lower limits of analysis are discussed. New and improved precise methods of analysis for low level (<1 mg/L) measurement of oxychlorine species including chlorate and chlorite ions are given. Advantages and disadvantages of speciation are noted.

A modified iodometric method is reported to measure chlorate ion concentration down to the sub-mg/L level with high precision and accuracy. Hexane and nitrogen are used as shielding agents to isolate the sample solution from the air phase to prevent air oxidation of iodide ion. Chlorate ion is reduced by iodide ion in 6M hydrochloric acid. By the addition of saturated sodium phosphate, the hydrogen ion concentration is lowered to approximately 3M, and the liberated iodine is titrated with standard sodium thiosulfate solution. The endpoint is detected using Thyodene as the indicator or by the color of iodine in the hexane layer. A potentiometric endpoint is recommended for the determination of chlorate ion at concentrations less than 1.0×10^{-4} N (3.5 mg/L reported as chlorine). By this modified iodometric method, the chlorate ion down to the sub-mg/L level can be determined with a precision of better than ±1% with a lower detection limit of 0.1 mg/L. The method is proposed as a standard baseline method of analysis.

An analytical method is reported to determine hypochlorite, chlorite, and chlorate ions in a mixture at the sub-mg/L level. Chlorate ion is determined directly by a modified iodometric method in which hexane along with nitrogen gas is used as a shielding agent to isolate the sample solution from the air phase to prevent air oxidation of iodide ion. A saturated sodium phosphate solution is used to partially neutralize the acidic sample solution just before titrating. Chlorite ion is determined directly by the modified Suzuki-Gordon method where free residual chlorine (chlorine and hypochlorous acid) is converted to hypochlorite ion which in the mixture is reduced to chloride ion by sulfite ion at pH 10.5. Following this oxidation, the chlorite ion followed by the oxidation of excess sulfite ion by iodine is reduced to chloride ion by iodide ion at pH 2. Hypochlorite ion is determined indirectly from the results of the modified iodometric method and the modified Suzuki-Gordon method. The titration endpoint is determined directly from the first derivative titration curve obtained by a potentiometric method. The overall precision is ±3% for oxychlorine species at concentrations in the range of 0.3 - 100 mg/L with lower detection limits of 0.1 mg/L.

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SECTION I

INTRODUCTION

Methods for the chemical analysis of solutions of the chlorine-containing oxidizing agents above the 3 mg/L level appear to be well defined in the chemical literature (1-30). In the 1979 update of "Drinking Water and Health," the National Academy of Science estimated acceptable exposure values of 0.38 mg/L for chlorine dioxide and 0.21 mg/L for chlorite ion. Later in 1979, the Federal Register (31) published recommendations which should be placed on the level of residual oxidants such as chlorine dioxide, chlorite ion and chlorate ion which result from the chlorine dioxide treatment of water to be used as drinking water. The Federal Register also reports " . . . whenever chlorine dioxide is used residual oxidants should be monitored and kept below 0.5 mg/L. The EPA will consider establishing an MCL for chlorine dioxide, chlorite ion and chlorate ion or the aggregate as total oxidant for inclusion in the Revised Regulations after further studies have been fully evaluated . . . ".

In this context, it should be noted that in early 1980 none of the analytical techniques in the literature for the analysis of chlorine-containing oxidizing agents were capable of routinely determining chlorate ion concentrations at the sub-mg/L level. The purpose of this report is to describe the underlying chemical reactions and interactions of the oxychlorine species and to present improved methodology which provides for the analysis of chlorate ion in drinking water at levels down to 0.1 mg/L. In addition, data are presented for the speciation of chlorate ions along with chlorine dioxide, chlorite ions and free chlorine (hypochlorous acid plus chlorine). The speciation techniques provide an accuracy and precision of better than ±3% and should provide an important standard baseline technique for comparison of other possibly more rapid, more highly automated routine methods of analysis. Prior to this project, no such baseline comparison techniques were available.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

1. Determination of Chlorate Ions down to the Sub-mg/L Level.

This is made possible by a modified iodometric method in which hexane and nitrogen gas are used as shielding agents to prevent air oxidation of iodide ion. Chlorate ion is reduced by iodide ion in 6 M hydrochloric acid. In addition, saturated sodium phosphate solution is used to partially neutralize the acidic sample solution prior to the actual titration. The liberated iodine is titrated with standard thiosulfate solution. The endpoint is detected potentiometrically. The precision is better than ±1% down to the sub-mg/L level.

2. Determination of Mixtures of Chlorate and Chlorite Ions.

The concentrations of chlorite ion and chlorate ion are determined directly and continuously on a single sample thus minimizing cumulative errors. Two successive titrations are followed potentiometrically with an internal precision and accuracy of the titrations of better than ±2%.

3. Determination of Hypochlorite, Chlorite and Chlorate Ions in Mixtures at the Sub-mg/L Level.

An analytical method is reported to determine hypochlorite, chlorite, and chlorate ions in a mixture down to the sub-mg/L level. Chlorate ion is determined directly by a modified iodometric method in which hexane along with nitrogen gas is used as a shielding agent to isolate the sample solution from the air phase to prevent air oxidation of iodide ion. Chlorite ion is also determined directly by the modified Suzuki-Gordon method where only hypochlorite ion in the mixture is reduced to chloride ion by sulfite ion at pH 10.5 followed by oxidation of excess sulfite ion by iodine. Hypochlorite ion is determined indirectly from the results of the modified iodometric method and the modified Suzuki-Gordon method. The titration endpoint is determined directly from the first derivative titration curve obtained by a potentiometric method. The overall precision is ±3% for oxychlorine species at concentrations in the range of 0.3 - 100 mg/L. Lower detection limits of 0.1 mg/L can be achieved, however.

4. Endpoint Determination.

The potentiometric titration method is recommended for each of the determinations at low concentration levels (especially below 1 mg/L) because the blank is relatively small and no subjectivity by the investigator is involved.

SECTION 3

LITERATURE BACKGROUND

The 14th edition of Standard Methods (1) describes in detail eight methods for residual free chlorine ($HOCl + OC^- + Cl_2$) analysis. In general, these methods describe procedures for the determination of the total oxidizing power of the solution and can be readily modified for the determination of aggregate chlorine-containing species including chlorite ion, chlorine dioxide, and chlorate ion along with other species such as Cl_2O (the anhydride of hypochlorous acid) and the like.

As a matter of convenience, these methods can be categorized as iodometric (or modified iodometric) methods, colorimetric methods, chromatographic techniques, and specialized instrumental/electrode techniques--or various combinations of the above--each with specific advantages or disadvantages.

The eight methods for free chlorine residual analysis described in Standard Methods include two iodometric methods, Phenylarsine oxide-amperometric titration, Stabilized Neutral Orthotolidine, N,N-diethyl-p-diphenyldiaamine (DPD)-Ferrous Ion Titration, DPD Colorimetric, Leuco Crystal Violet, and Syringaldazine. Details of these methods are given in the "State of the Art" compilation by Simons (32) and the "Comparison of Methods" by Bender (33). The relative usefulness of each method along with descriptions of known interferences such as turbidity, organic matter, ionic materials, solids, color, buffering capacity as well as the nature of the sample and the time between collection of the sample and the actual analysis are described in the Standard Methods (1). It must be emphasized, however, that each of these methods is based on the total oxidizing capacity of the solution being analyzed and is readily subject to interferences from the presence of other potential oxidizing agents and/or intermediates from concomitant chemical reactions. Under ideal conditions some of the methods are accurate to better than ±1%--especially in the absence of common interferences--whereas others of the methods are almost semi-quantitative in nature with many common species interfering with both the precision and accuracy of the measurements. Typical of the species most difficult to analyze is chlorate ion at levels below 3 mg/L where the published methods indicate reliability ranging from 25-50%.

Improved analytical techniques and/or methodology require a detailed understanding of the potential reactions and interactions of the species under investigation as well as the chemistry of various intermediates associated with the analyses under consideration. For example, the detailed analyses of solutions containing chlorine or hypochlorous acid along with chlorite ion at pH 2 or pH 7 or pH 10 are indeed quite different in that the reaction between residual free chlorine (Cl_2 and/or HOCl) with chlorite ion varies markedly as

a function of pH--being very rapid at pH 2 and almost negligible at pH 10. Likewise, the self-disproportionation of chlorine dioxide is almost instantaneous at pH 12 whereas it is infinitesimally slow at pH 4. Without a detailed understanding of reactions and interactions such as these, the validity of the methods themselves may be suspect and the reported analyses might be in considerable error owing to various side-reactions and interactions.

Another way of stating the problem is to emphasize the fact that, analytical chemistry is a problem solving process--not just the pushing of buttons, or reading titration volumes, or measuring slopes of titration curves. A slightly paraphrased statement by H. C. Laitinen (34) seems to apply directly: ". . . the (un)scientific method is not a step-by-step process--BUT requires good experimental design . . . ingenuity or originality and (chemical intuition) . . ."

Thus, several details with respect to the reactions and interactions of hydrogen ion or chlorine and/or hypochlorous acid with chlorite ion along with the disproportionation of chlorine dioxide itself must be considered before discussing in any detail the potential modifications of existing analytical procedures.

Chlorite ion in drinking water or wastewater below pH 4 is relatively unstable as a result of the acid-catalyzed disproportionation of chlorite ion to form chlorine dioxide, chlorate ion and chloride ion. Likewise, chlorite ion in the presence of hypochlorous acid and/or chlorine below pH 8 also reacts to form chlorine dioxide, chlorate ion and chloride ion (35). For example, the reactions given below:

$$Cl_2 + 2\ ClO_2^- \rightarrow 2\ ClO_2 + 2\ Cl^- \quad (1)$$

$$3\ Cl_2 + 4\ ClO_2^- + 2\ H_2O \rightarrow 2\ ClO_3^- + 2\ ClO_2 + 6\ Cl^- + 4\ H^+ \quad (2)$$

$$Cl_2 + ClO_2^- + H_2O \rightarrow ClO_3^- + 2Cl^- + 2\ H^+ \quad (3)$$

describe the various ratios of chlorine dioxide to chlorate ion which can be formed as a result of the residual free chlorine (chlorine plus hypochlorous acid) reaction with chlorite ion. The reaction can be forced to produce only chlorine dioxide (as shown in equation 1) as it is in many water treatment plants by the direct reaction of chlorine and/or hypochlorous acid with sodium chlorite. On the other hand, in dilute solution in the pH 1-3 range more than 90% chlorate ion can be formed. A summary of these results is shown in Table 1. Furthermore, at pH 1, the reaction shown by equation 1 is virtually instantaneous (the half-life is approximately 10-20 sec) and at pH 7 with solutions containing 1 mg/L of each reactant the reaction proceeds slowly such that the half-life is on the order of 10-20 minutes. A summary of these results is shown in Table 2. Clearly, these effects must be taken into account in any chemical analysis or speciation scheme.

Table 1. The Reaction of Sodium Chlorite With Chlorine and/or Hypochlorous Acid

Initial* $NaClO_2$ (mg/L)	% ClO_2 formed	% ClO_3^- formed
900	90	10
300	82	18
30	54	46
10	30	70
1.0	<10	>90

*Calculated in terms of mg/L residual chlorine. Measured at pH 1 with a 2:1 molar ratio of $NaClO_2$ to Cl_2 or HOCl

Table 2. Rate Constants at 25° for the Oxidation of Sodium Chlorite by Residual Chlorine at pH 2.5

mg/L $NaClO_2$	mg/L HOCl	half-life (seconds)
5	3	~60
25	15	3.5
1500	8	<1.0

The self-disproportionation of chlorous acid or sodium chlorite in acid solution must also be considered. This has been studied in considerable detail at various ionic strengths under a variety of hydrogen ion conditions ranging from 10^{-4} M (pH 4) to 2 M and with up to 0.1 M added chloride ion (36-38). In the absence of added chloride ion, in 1.2 and 2 M perchloric acid at 25°, the stoichiometry can be approximated as:

$$4\ ClO_2^- + 2\ H^+ \rightarrow 2\ ClO_2 + ClO_3^- + Cl^- + H_2O \qquad (4)$$

At the beginning of the reaction less chlorine dioxide than that predicted by equation 4 is formed. As the reaction proceeds, the relative amount of chlorine dioxide produced increases. The relative amount of chlorine dioxide produced also varies with the hydrogen ion concentration. Chloride ion catalyzes the disproportionation of chlorous acid and also alters the stoichiometry to approximately:

$$5\ HClO_2 \rightarrow 4\ ClO_2 + Cl^- + H^+ + 2\ H_2O \qquad (5)$$

As the reaction proceeds in the presence of initial chloride ion, less chlorine dioxide than that predicted by equation 5 is formed. Also, as the initial concentration of chloride ion is decreased the relative amount of chlorine dioxide formed also decreases. The reaction is relatively rapid especially on a water purification time schedule such as might be encountered in water treatment plant: for example, at pH 2.5 more than 20% of the chlorite ion undergoes self-disproportionation in less than 10 minutes.

Detailed kinetic studies (37) have shown that in the absence of initially present chloride ion the overall reaction is second order in chlorous acid whereas in the presence of chloride ion, the reaction becomes first order in chlorous acid. The rate law for the self-disproportionation of chlorous acid as reported by Kieffer and Gordon (37) is given below:

$$\frac{-d[HClO_2]}{dt} = k_1[HClO_2]^2 + \frac{k_2[HClO_2][Cl^-]^2}{K + [Cl^-]} \qquad (6)$$

The parameters k_1 and K are independent of the hydrogen ion concentration and correspond to $1.2 \times 10^{-2}\ M^{-1}\ s^{-1}$ and 0.0012 M, respectively. In solutions which contain 1 M $HClO_4$, k_2 is $1.5 \times 10^{-2}\ M^{-1}\ s^{-1}$, and in 2 M $HClO_4$, k_2 is $3.0 \times 10^{-2}\ M^{-1}\ s^{-1}$.

These results can be interpreted in terms of the following mechanism.

Path 1: uncatalyzed

$$HClO_2 + HClO_2 \xrightarrow{k_1} HOCl + H^+ + ClO_3^- \qquad \text{(rate determining)}$$

$$HOCl + HClO_2 \rightarrow [Cl\text{-}Cl{<}^{O}_{O}] + H_2O$$

$$HOCl + H^+ + Cl^- \rightarrow Cl_2 + H_2O$$

$$Cl_2 + HClO_2 \rightarrow [Cl\text{-}Cl{<}^{O}_{O}] + H^+ + Cl^-$$

$$[Cl\text{-}Cl{<}^{O}_{O}] + H_2O \rightarrow Cl^- + ClO_3^- + 2H^+$$

$$2[Cl\text{-}Cl{<}^{O}_{O}] \rightarrow Cl_2 + 2ClO_2$$

Path 2: chloride ion catalyzed

$$HClO_2 + Cl^- \underset{}{\overset{K^{-1}}{\rightleftharpoons}} [HCl_2O_2^-]$$

$$[HCl_2O_2^-] + Cl^- \overset{k_2}{\rightarrow} \text{products (rate determining)}$$

Path 3: uncatalyzed--low hydrogen ion

$$HClO_2 + ClO_2^- \rightarrow [HClO_2\text{-}ClO_2^-]^* \rightarrow \text{products}$$

The initial rate of formation of chlorine dioxide appears to correspond to the relative amounts of chlorite ion and chlorous acid present, i.e., the maximum production of chlorine dioxide occurs approximately at the pK_a of chlorous acid (pK_a = 2.31). These observations suggest a third pathway in the mechanism shown above. This term in the rate law involves the reaction of chlorite ion and chlorous acid to form an intermediate of the composition ($HClO_2 \cdot ClO_2^-$). The observations here suggest that the intermediate $[Cl_2O_2]$ produces chlorine dioxide more rapidly in the low acid region than does either the first or the second pathway shown above in the proposed mechanism. A detailed understanding of the above mechanism and the observed rate laws for both the self-disproportionation of chlorite ion and the reactions/interactions of chlorite ion with residual chlorine is the key to understanding the conditions under which or the ease with which speciation of the various oxychlorine moities can be achieved.

Finally, the base catalyzed self-decomposition of chlorine dioxide

$$2\ ClO_2 + 2\ OH^- \rightarrow ClO_2^- + ClO_3^- + H_2O \qquad (7)$$

must also be taken into account because both chlorate ion and chlorite ion can be formed thus potentially complicating speciation or aggregate measurements.

Many reports appear in the literature (7,9,39) describing the self-decomposition of chlorine dioxide as a function of pH. Although there is good agreement that equation 7 correctly describes the stoichiometry, there is considerable disagreement with respect to the details of the rate law and mechanism associated with the decomposition process itself. Variations include first order and second order terms with the role of hydroxide ion and other bases being somewhat unclear.

A recent study by Emerich (39) clearly indicates that the rate of the reaction is markedly dependent on the chlorine dioxide concentration as well as hydroxide ion or any other base such as phosphate ion, carbonate ion, borate ion and the like. A summary of typical differences observed with various bases other than hydroxide ion are shown in Table 3. Typical half-lives for the rate of chlorine dioxide self-decomposition catalyzed by hydroxide ion but in the absence of other bases are given in Table 4.

Table 3. Buffer Effects on the Rate of Self-Decomposition of Solutions Containing 10 mg/L Chlorine Dioxide at pH 10

	k_1 (sec^{-1})
carbonate buffer	2.4×10^{-4}
phosphate buffer	1.1×10^{-4}
borate buffer	0.17×10^{-4}

Table 4. Self-Decomposition of Chlorine Dioxide in Basic Solution at 25° with 10 mg/L Chlorine Dioxide

pH	half-life (seconds)
13	300
12.7	520
12.4	920
12.1	1380

The data in the literature and the recent study by Emerich (39) are consistent with the following mechanism

$$ClO_2 + \text{Base} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [\text{Intermediate}]$$

$$ClO_2 + \text{Intermediate} \xrightarrow{k_2} ClO_2^- + ClO_3^-$$

$$ClO_2 \xrightarrow{k_o} \text{zero order loss of } ClO_2$$

Thus, at high concentrations of chlorine dioxide the process becomes pseudo first order in chlorine dioxide and markedly dependent on the concentration and type of base and/or anion present in the solution under consideration. Once again, clearly these effects cannot be neglected.

The iodometric method has been used widely to measure the concentration of various cations and anions (3,4). Oxychlorine species such as hypochlorite ion and/or hypochlorous acid and chlorite ion can be measured by the iodometric method accurately and precisely (4). However, the reaction of chlorate ion with iodide ion is slow under mildly acidic conditions:

$$ClO_3^- + 6I^- + 6H^+ \rightarrow 3I_2 + Cl^- + 3H_2O \qquad (8)$$

According to Bray (40), the rate of the reaction 1 is proportional to the chlorate ion concentration and the square of the hydrogen ion concentration, and is a linear function of the concentrations of chloride and iodide ions. A recent study by Hadjiioannou and coworkers (41) suggests that the reaction obeys the following rate law

$$-d[ClO_3^-]/dt = k[ClO_3^-][I^-]^{1.5}[H^+]^2 \qquad (9)$$

where k is 35 ± 1.0 $M^{-3.5}s^{-1}$ at 30°C and ionic strength 1.0 M.

Thus, normally the quantitative iodometric determination of chlorate ion is possible in the presence of a large excess of hydrochloric acid. Unfortunately, under these conditions iodide ion is readily oxidized by air:

$$4I^- + 4H^+ + O_2 \rightarrow 2I_2 + 2H_2O \qquad (10)$$

Under these conditions, relatively large errors for chlorate ion determinations on the order of 10-20% or greater are noted at the mg/L level. In the literature, various modifications have suggested displacement of air by carbon dioxide or nitrogen or the use of bromide ion in the presence of 7.5 M hydrochloric acid to reduce chlorate ion. In the latter case, the bromine produced is also determined iodometrically. However, each of these modifications is primarily applicable to the determination of chlorate ion in relatively high concentrations, namely well above the 3 mg/L level.

Kolthoff (4) has suggested that removal of air from the sample solution by using sodium carbonate is effective to prevent the air oxidation of iodide ion. Ditz (42) and Rupp (43) have suggested using bromide ion in the presence of 7.5 M hydrochloric acid to reduce chlorate ion. The bromine produced thereby is determined iodometrically. However, these modified iodometric methods are primarily applicable to the determination of chlorate ion in the relatively high concentration range (above 0.02 N or 700 mg/L). For the determination of chlorate ion in concentrations such as in the millimolar

and sub-millimolar range, additional modifications of the iodometric method are necessary in order to avoid the air oxidation of iodide ion (5,10,40).

A recent study (44) has suggested that hexane is an effective shielding agent to prevent the air oxidation of iodide ion, and that the interference from air oxidation can be minimized when chlorate ion is reduced by iodide ion in 6 M hydrochloric acid followed by neutralization to approximately 3 M with either 50% (w/w) sodium hydroxide or solid sodium phosphate (Na_2HPO_4).

In a previous study, Prince (11) reported a spectrophotometric method where the analysis of chlorate ion requires at least a four hour reaction period. Another spectrophotometric method described by Chen (12) utilized either ferrous ion or iodide ion as a reductant for chlorite ion and chlorate ion. The chloride ion formed is determined spectrophotometrically by the mercuric chloranilate technique (27). However, chlorite ion interferes with this technique in that chloranilic acid is liberated in a nonquantitative way.

Hong and Rapson (15) have reported a method which iodometrically measures chlorate ion in chlorine oxidant mixtures in a strongly acidic medium, although it is well known that air oxidation of iodide ion takes place under the conditions reported (4). This method is limited to concentrations above 2×10^{-2} M oxidant.

Yamasaki, Ohura, and Nakamori (16) have analyzed mixtures of chlorine-containing oxidants in the concentration range above 5×10^{-4} M by using a short-circuit amperometric titration method. In this method, sodium arsenite, potassium borohydride, and sulfurous acid are used as reductants for hypochlorite, chlorite, and chlorate ions, respectively.

Tang and Gordon (5) have determined chloride, chlorite, and chlorate ions in mixtures at the concentration level of 1×10^{-3} M by using successive potentiometric titrations in which chlorite and chlorate ions are selectively reduced to chloride ion by arsenic(III) oxide in the presence of osmium tetraoxide as catalyst in 70% (V/V) methanol medium. The concentration of chloride ion formed is determined potentiometrically by using a chloride ion selective electrode.

It should be noted, however, that the methods described above are not applicable to the determination of the chlorine-containing oxidants in mixtures at low concentrations such as at the sub-mg/L level (45) even under the most ideal conditions--especially if the mixture contains chlorate ion.

Recently, Gordon and Ikeda reported a modified iodometric method (46,47) which makes it possible to measure concentrations of chlorate ion at the sub-mg/L level. In that method, hexane and nitrogen are used as shielding agents to prevent the air-oxidation of iodide ion. Furthermore, chlorate ion is reduced by iodide ion in 6 M hydrochloric acid followed by partial neutralization with saturated sodium phosphate solution. Finally, Suzuki and Gordon (6) have devised a method which measures chlorite ion directly in the presence of excess hypochlorous acid or hypochlorite ion.

SECTION 4

EXPERIMENTAL PROCEDURES

Reagent grade chemicals and deionized distilled water were used throughout. Hypochlorous acid solutions were obtained by hydrolysis of Cl_2O. A solution of Cl_2O in CCl_4 was prepared by the Cady method (49). A sodium hypochlorite stock solution was obtained by neutralizing a hypochlorous acid solution with aqueous sodium hydroxide and was stored in a refrigerator. The concentration of this stock solution was determined iodometrically (4). Dilute solutions (1×10^{-4} N and 1×10^{-5} N) were prepared daily by diluting the stock solution. The sodium chlorite (Matheson Coleman and Bell) stock solution was stored in an aluminum foil covered bottle and was freshly prepared before each experiment. Potassium chlorate (Matheson Coleman and Bell) was recrystallized from triple distilled water and was dried at 120°C.

Sodium thiosulfate solution (5×10^{-4} N) was prepared in freshly boiled and cooled distilled water and was stored in an aluminum foil covered bottle. The solution was standardized with primary standard potassium iodate solution. Potassium iodide and potassium iodate (Matheson Coleman and Bell) were used without further purification. Saturated sodium phosphate solution was prepared by dissolving as much $Na_2HPO_4 \cdot 12H_2O$ as possible (Matheson Coleman and Bell) in 500-mL of hot deionized distilled water. Borate buffer solution (pH 10.5) was prepared by mixing 113.5 mL of 0.1 M sodium hydroxide, 250 mL of 0.025 M sodium borate (Fisher Scientific Company) and deionized distilled water in a 500-mL volumetric flask. Sodium sulfite (Fisher Scientific Company) was used without further purification. An iodine solution of 0.002 M was prepared by mixing 0.13 g of iodine, 0.40 g potassium iodide and deionized distilled water in a 250-mL volumetric flask. The solution was stored in a brown glass-stoppered bottle and refrigerated. Spectroanalyzed grade hexane (Fisher Scientific Company) was used without further purification. The nitrogen gas used for deaeration was passed through a scrubber containing 0.1 M chromium(II) in 1.0 M H_2SO_4 to remove traces of oxygen.

The iodometric endpoint was detected with either Thyodene as the indicator or potentiometrically. The sodium thiosulfate solution was titrated by using a Metrohm Herisau E535 auto-buret. For the potentiometric endpoint, a combination redox electrode as shown in Figure 1 and a Metrohm Herisau Model E536 potentiometer were used. Sodium thiosulfate solution was titrated at the speed of 0.05 mL/min.

For each experiment, appropriate blank experiments were carried out for solutions of the same composition as the sample solution except that the deionized distilled water was used instead of known amounts of the chlorine-containing oxidizing agents.

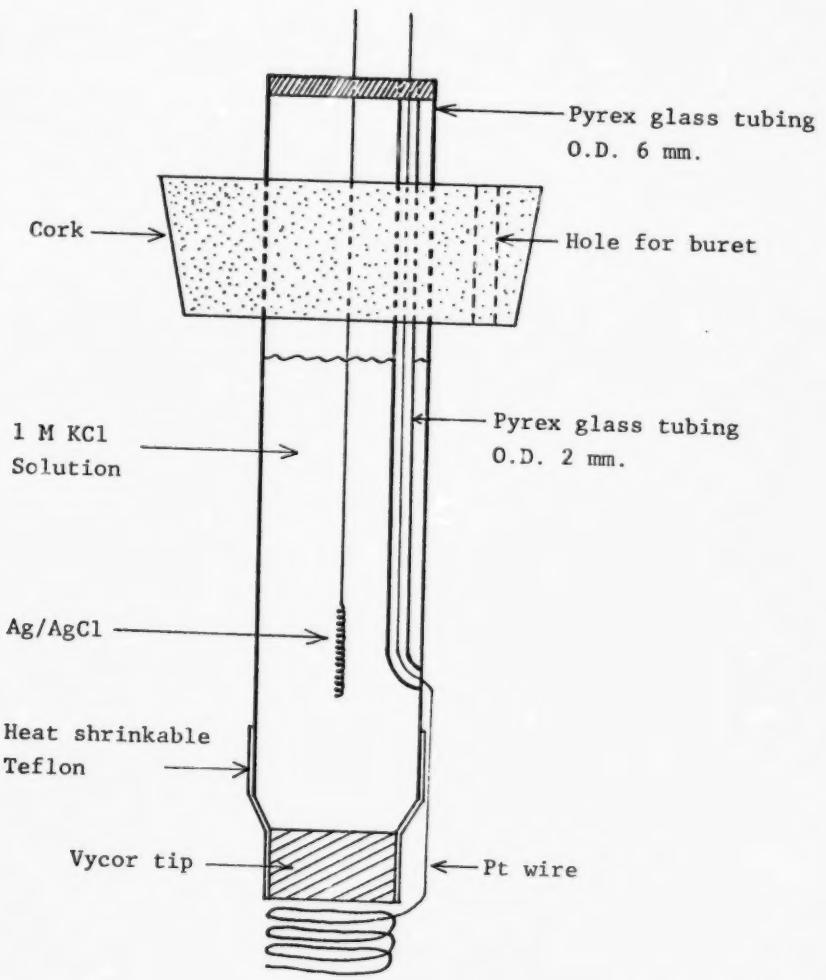

Figure 1. Combination redox electrode

SECTION 5

RESULTS AND DISCUSSION

Analysis of Chlorate Ion

The iodometric method has been used widely to determine the concentration of various cations and anions. All of the previous iodometric methods reported in the literature (1,2) tend to suffer from the difficulty of high and relatively nonreproducible blank corrections resulting in imprecise and usually inaccurate low level chlorate ion determinations. During our earlier studies of various reactions and interactions of the oxychlorine species it was necessary to develop a simple, direct method (5) for the quantitative determination of chloride, chlorite, and chlorate ions in the presence of each other. In this method, samples are titrated with standard silver nitrate solution in 70% (V/V) methanol and a combination chloride ion selective electrode is employed for the potentiometric endpoint detection. The chloride ion concentration corresponds to the first potentiometric endpoint. Chlorite ion is reduced to form chloride ion in the neutral pH range by using arsenic(III) and 0.005% osmium tetroxide as a catalyst. The chloride ion formed is titrated to the second potentiometric endpoint. Finally, chlorate ion is reduced to chloride ion by acidification to 1 M with sulfuric acid and by using 0.1% osmium tetroxide as the continuing catalyst. Chloride ion formed is titrated to a third potentiometric endpoint. The precision of the method is better than ±2% in the high concentration level (10-100 mg/L chlorate ion) and the results are in good agreement with other methods where comparisons can be made. The advantages of the Tang-Gordon method include elimination of air oxidation and a direct comparison of a chlorine balance with the redox balance in solutions containing mixtures of the oxychlorine species. Attempts to extend this method down to the sub-mg/L level were unsuccessful resulting in relative errors in the range of 10-20% with considerable variability between samples and between individual investigators.

In the Tang modified iodometric method (5,44), solid sodium phosphate and 50% (w/w) sodium hydroxide were used as neutralizing agents. However, a marked disadvantage of this method is that sodium phosphate does not dissolve rapidly into the sample solution and the addition of 50% sodium hydroxide generates a large amount of heat during the neutralization process. In this report, a saturated sodium phosphate solution was used instead of the above mixture and hexane was used as a shielding agent.

The measurement of chlorate ion at various concentration levels with thyodene as the indicator was carried out as follows: The sample was prepared by using a Silverman syringe (48) to deliver the known volumes of the standard reference potassium chlorate solution into a 60 mL glass-stoppered

flask. To this sample solution, 0.25 mL of potassium iodide was added and the concentration varied from 0.3 M to 0.06 M depending on the chlorate ion concentration (0.1 N -1.0 x 10^{-4} N). This solution was bubbled with nitrogen gas for 10 minutes. After deaeration, approximately 1 mL of hexane was added to the sample solution. Deaerated concentrated hydrochloric acid was added to the sample solution to adjust it to 6 M in acid and immediately the flask was stoppered. After the reaction was complete (normally 20 minutes), deaerated saturated sodium phosphate solution was added to the sample solution to reduce the acidity to ~3 M. Finally, the liberated iodine was titrated with standard sodium thiosulfate solution and an appropriate amount of Thyodene solution was added when the yellow color of iodine in aqueous phase became pale. For concentrated solutions, the thyodene color change was used to determine the endpoint. In the more dilute solutions, the titration endpoint was determined by comparing the color of the hexane layer of the sample solution with that of a blank solution consisting of only water and hexane. The reddish-violet color of iodine in the hexane layer makes it easier to detect a titration endpoint because the limit of visibility of the color of hexane layer exceeds that of the Thyodene-iodine color. In each experiment, blank corrections were made for solutions of the same composition as that of the sample solution except that deionized distilled water was used in place of the potassium chlorate solution.

The results are shown in Table 5 and indicate that the determination of chlorate ion in concentrations (45) greater than 1.0 x 10^{-4} N (3.5 mg/L as residual free chlorine) is possible by using this modified iodometric method--with appropriate blank corrections. In these experiments, time-dependent measurements show that chlorate ion is quantitatively reduced by iodide ion within 20 minutes. Furthermore, the blank volume correction was 0.0 - 5.0% of the sample titration volume, depending on specific reaction conditions. This result indicates that the air oxidation of iodide ion is effectively minimized by using hexane as a shielding agent and by neutralization of the sample solution by the addition of a deaerated saturated solution of sodium phosphate.

On the basis of these results, the determination of chlorate ion at the level of 1.0 x 10^{-5} N (0.35 mg/L as residual free chlorine) was studied by using the same procedure (45). However, the color of iodine in the hexane layer is a very pale pink at this concentration level, and hence the endpoint could not be detected correctly and reproducibly. Benzene was tried as a replacement for hexane because the color of iodine in a benzene layer is more intense than in hexane. The difference in color intensity is primarily due to the fact that benzene can extract iodine more efficiently than hexane. As is shown in Table 6, chlorate ion at the level of 1.0 x 10^{-5} N can be determined by this method using benzene as a shielding agent. However, this modification has the disadvantage that the endpoint determination is difficult and tends to depend on the investigator resulting in possible operator bias, and benzene is a potentially hazardous solvent.

Because of the disadvantages inherent in the optical endpoint methods described above for more concentrated solutions containing chlorate ion (> 1.0 x 10^{-4} N ClO_3^-), the potentiometric titration method was modified and is also reported here. The effect of hexane as a shielding agent on the potentio-

Table 5. Determination of Chlorate Ion by the Modified Iodometric Method Using Hexane as a Shielding Agent

Sample	Equiv/L ClO_3^- added	Equiv/L ClO_3^- found [a]	% Error
1	1.002×10^{-1}	$(1.007 \pm 0.001) \times 10^{-1}$	0.5 ± 0.1
2	1.031×10^{-2}	$(1.033 \pm 0.005) \times 10^{-2}$	0.2 ± 0.5
3	5.035×10^{-3}	$(5.03 \pm 0.08) \times 10^{-3}$	0.1 ± 0.6
4	2.609×10^{-3}	$(2.60 \pm 0.03) \times 10^{-3}$	0.4 ± 0.5
5	6.194×10^{-4}	$(6.21 \pm 0.07) \times 10^{-4}$	0.2 ± 0.8
6	1.011×10^{-4}	$(1.00 \pm 0.02) \times 10^{-4}$	1.1 ± 1.0

[a] The uncertainties represent the standard deviation from the mean for eight replicate samples except for samples 3 and 5 which consisted of nine replicates.

Table 6. Determination of Chlorate Ion at the sub-mg/L Level [a]

Method	Shielding Agent	Equiv/L ClO_3^- added $\times 10^{-5}$	Equiv/L ClO_3^- found $\times 10^{-5}$	% Error
Optical endpoint	benzene	1.011	1.018 ± 0.094	0.7 ± 1.0
Potentiometric titration	hexane	1.011	1.019 ± 0.036	0.8 ± 0.6
Potentiometric titration	N_2 gas	1.011	1.023 ± 0.051	1.2 ± 1.0

[a] The uncertainties represent the standard deviation from the mean for eight replicate titrations.

metric endpoint detection was evaluated by standardizing the sodium thiosulfate solution with known volumes of potassium iodate solution which had been prepared by weight. Samples were prepared by delivering an exact volume (48) of potassium iodate solution (4.239×10^{-4} N) into a 60 mL glass-stoppered flask with a Silverman syringe. An appropriate amount of 0.03 M potassium iodide solution was added and the sample was acidified with 1 M hydrochloric acid to a pH less than 2. Approximately 1 mL of hexane was added and the combination redox electrode (Figure 1) was immersed under the hexane layer. The liberated iodine was titrated with sodium thiosulfate solution at a delivery speed of 0.05 mL/min. The endpoint was determined directly from the maximum of the first derivative titration curve as shown in Figure 2. The results in Table 7 for the standardization with and without hexane shielding of the sample are indistinguishable within experimental error. This result indicates that the hexane shielding has no measurable effect on the potentiometric endpoint.

Table 7. Standardization of Sodium Thiofulfate Solution with and without Hexane Using Potentiometric Endpoint Detection

Sample 1 [a] $[S_2O_3^{2-}]/10^{-4}$ N	Sample 2 [b] $[S_2O_3^{2-}]/10^{-4}$ N
5.213	5.272
5.335	5.302
5.267	5.319
5.292	5.320
5.232	5.309
Mean [c]: 5.268 ± 0.048	5.304 ± 0.020

[a] Sample consists of 5.0066 mL of 4.239×10^{-4} N KIO_3, 0.5 mL of 0.03 M KI, and 1 mL hexane, and 2 mL of 1 M HCl.

[b] Sample consists of 5.0066 mL of 4.239×10^{-4} N KIO_3, 0.5 mL of 0.03 M KI, and 2 mL of 1 M HCl (no hexane added).

[c] The uncertainties represent the standard deviation from the mean.

Chlorate ion concentrations (45) at the level of 1.0×10^{-5} N (0.35 mg/L) were analyzed by the potentiometric method according to the same procedure as described earlier. Exactly 10.013_2 mL of potassium chlorate stock solution

and 0.5 mL of 0.015 M potassium iodide solution were used. Twelve mL of deaerated hydrochloric acid and 23 mL of the deaerated saturated sodium phosphate solution were added for acidification and neutralization of sample, respectively. Under these conditions of lower chlorate ion concentration, the reaction between chlorate ion and iodide ion requires 40 minutes for completion. The end-point was detected from the first derivative titration curve. A typical end-point is shown in Figure 2. Furthermore, the same method was investigated by using nitrogen gas rather than a layer of hexane as a shielding agent. In this method, the air space of sample flask was filled with nitrogen gas immediately after the deaerated saturated sodium phosphate solution was added to the sample solution. In both methods, blank corrections were made for solutions of the same composition as the sample solution except for using the deionized distilled water instead of potassium chlorate solution. At these low concentration levels, the blank volumes were nominally 20% and 30% of the sample titration volumes in the hexane shielding and nitrogen gas shielding experiments, respectively. This result shows that the shielding effect of nitrogen gas is less effective than that of hexane. However, and most importantly, as is noted in Table 6, with appropriate blank corrections and careful shielding it is possible to accurately measure chlorate ion down to the sub-mg/L level by the potentiometric method.

Speciation and Aggregate Analysis

When chlorine dioxide is used for the treatment of water, chlorate and chlorite ions are always present as potential by-products. Speciation or aggreate measurements frequently depend on the measurement of small differences with the most difficult species invariably being determined by the difference of differences. This may result in considerable accumulated error and can contribute to major differences in results between investigators and between individual laboratories--thus affecting the reported accuracy of the measurements themselves. The modified method reported here can be used for speciation of chlorate ion, chlorite ion, and free chlorine (the aggregate of chlorine plus hypochlorous acid). The method can also be used directly for the concentration of chlorate ion and the aggregate concentration of all other species including chlorine dioxide, chlorite ion, and chlorine + hypochlorous acid.

In the method reported here, chlorate ion is directly determined by the modified iodometric method in which hexane is used as a shielding agent to isolate the sample solution from air. Chlorite ion is also determined directly by the Suzuki-Gordon method (6) where the chlorine and hypochlorous acid are all converted to hypochlorite ion. The hypochlorite ion in the mixture is reduced to chloride ion by sulfite ion at pH 10.5 followed by the oxidation of the excess sulfite ion by iodine. Following this oxidation, chlorite ion is reduced to chloride ion by iodide ion at pH 2 and determined directly by potentiometric titration. Hypochlorite ion is determined indirectly from the results of the modified iodometric method in the modified Suzuki-Gordon method. The titration endpoint is directly determined from the first derivative titration curve obtained by the potentiometric method. Typical results are shown in Table 6.

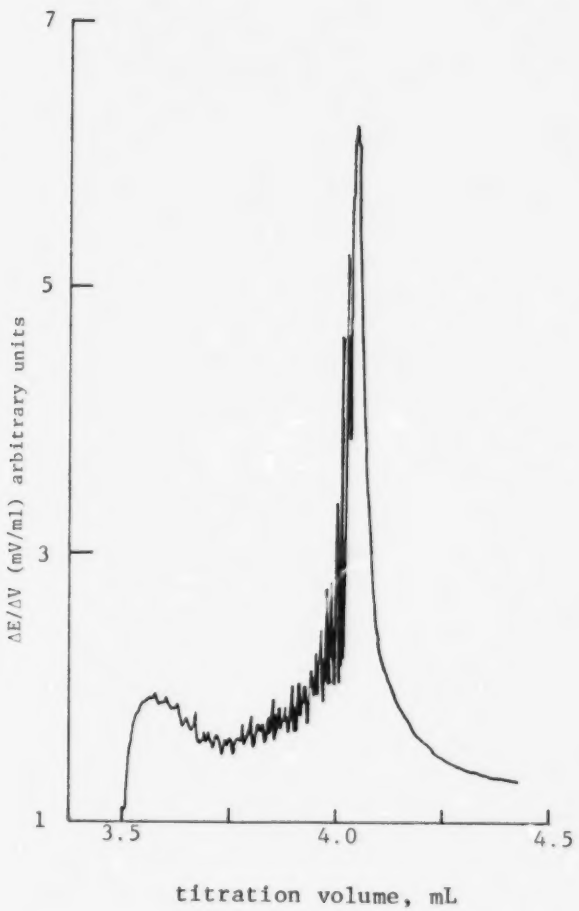

Figure 2. Derivative endpoint curve.

For the speciation and/or aggregate analysis of solutions containing chlorate ion, chlorite ion and chlorine + hypochlorous acid, the modified iodometric method and the Suzuki-Gordon method (6) were applied. The Suzuki-Gordon method is used to make possible the direct determination of chlorite ion even in the presence of excess hypochlorous acid and/or chlorine since frequently drinking water treated with chlorine dioxide and chlorine has such a composition. On this basis, the modified iodometric method is used to determine directly the concentration of chlorate ion after the reduction of hypochlorite ion and chlorite ion by iodide ion at pH 2. The hypochlorite ion concentration is determined indirectly from the results obtained by the Suzuki-Gordon method and the modified iodometric method reported here. This technique requires two sample solutions with a total of three titrations.

Determination of Chlorite and Chlorate Ions in Synthetic Mixtures.

For the analysis of this mixture, the procedure was developed based on two considerations: Chlorite ion is reduced to chloride ion by iodide ion at pH 2. Both chlorite ion and chlorate ion are reduced to chloride ion by iodide ion in 6 M hydrochloric acid. Hence, chlorite ion and chlorate ion in a mixture are determined by two independent titrations, where the normal iodometric method is used for the determination of the chlorite ion concentration and the modified iodometric method is applied for the determination of the total titration volume corresponding to the concentration of chlorite ion and chlorate ion. The endpoints in both cases are detected potentiometrically.

Two synthetic sample solutions (A and B) were prepared in 60-mL glass-stoppered flasks by delivering known volumes of sodium chlorite solution and potassium chlorate solution by using a Silverman syringe (24) which is accurate to better than 3/10,000 of a mL. In Sample A, 0.5 mL of 0.03 M potassium iodide solution is added and followed by acidification to approximately pH 2 by adding an appropriate volume of 0.5 M or 0.1 M hydrochloric acid. After the reaction is complete or in about 5 minutes, the redox electrode is immersed in the sample solution, and the liberated iodine is titrated with standard sodium thiosulfate solution (5.0×10^{-4}). The endpoint is detected directly from the first-derivative titration curve. This titration volume corresponds to the concentration of chlorite ion (in equivalents).

In Sample B, 0.5 mL of 0.03 M potassium iodide solution is added and followed by deaeration of the sample with nitrogen gas for 10 minutes. After deaeration, 1 mL hexane is added to the sample solution. An appropriate amount of deaerated hydrochloric acid is added to the sample solution to acidify it to approximately 6 M HCl, and immediately the flask is stoppered. After about 30 minutes, deaerated saturated sodium phosphate solution is added to partially neutralize the acidic sample solution. Finally, liberated iodine is titrated with standard sodium thiosulfate solution. The endpoint is again detected potentiometrically as described above. This titration volume corresponds to the total concentration of chlorite ion and chlorate ion (in equivalents). Hence, the concentration of chlorate ion is determined by subtracting the titration volume for Sample A from that for Sample B. The results are shown in Table 8.

Table 8. Determination of Chlorite and Chlorate Ions Concentrations in Synthetic Mixtures

Equiv/L ClO_2^- added x 10^{-5} N	Equiv/L ClO_2^- found [a] x 10^{-5} N	% ClO_3^- Recovery	Equiv/L ClO_3^- added x 10^{-5} N	Equiv/L ClO_3^- found‡ x 10^{-5} N	% ClO_3^- Recovery
Two Sample Technique					
9.877	9.95 ± 0.30	100.7	9.957	10.1 ± 0.7	101.4
4.230	4.19 ± 0.11	99.0	4.512	4.56 ± 0.2	101.1
2.589	2.60 ± 0.08	100.4	2.654	$2.64 \pm 0.1_2$	99.5
1.002	0.99 ± 0.01	98.8	9.957	$10.2_4 \pm 0.0_4$	102.8
Single Sample Method					
0.9613	0.955 ± 0.024	99.3	0.9957	0.983 ± 0.031	98.7
3.384	3.415 ± 0.072	100.9	0.9194	0.911 ± 0.028	99.1
0.9025	0.911 ± 0.021	100.9	3.948	$3.93_0 \pm 0.08_0$	99.5
1.763	1.751 ± 0.036	99.3	1.873	$1.89_1 \pm 0.04_5$	101.0

[a] The uncertainties represent the standard deviation from the mean for six replicate determinations.

‡ all numerals dropped below the line indicate less than total confidence in their absolute value, as determined.

Similar analyses were also carried out for samples which contained chlorite ion and chlorate ion down to the sub-mg/L level. In this case, potassium iodide solution of 0.015 M was used. The results are also shown in Table 8.

It is noted from the results in Table 8 that it is possible to determine the concentration of chlorite ion and chlorate ion in a mixture at the sub-mg/L level by using this two sample method. However, the precision for chlorate ion is relatively poor (~4%). This is due to the fact that the concentration of chlorate ion is obtained indirectly by subtracting the titration volume corresponding to chlorite ion concentration from the total titration volume corresponding to the concentration of chlorite ion and chlorate ion, and the associate individual titration errors. Furthermore, two identical sample solutions are necessary to determine the chlorate ion concentration by this method.

In order to improve those shortcomings, the following single sample method was developed. In this method, a single sample is prepared by the same procedure as that used in the first method. Immediately, 1 mL of 0.015 M potassium iodide solution is added to the sample solution, followed by adjusting the sample solution to approximately pH 2 by the addition of an appropriate volume of 0.5 M hydrochloric acid. After five minutes, the redox electrode is immersed in the sample, and the liberated iodine is titrated with standard sodium thiosulfate solution. The titration is stopped at the maximum point of the first-derivative titration curve for a dead-stop potentiometric endpoint. This titration volume corresponds to the concentration of chlorite ion (in equivalents).

At this point, the electrode is carefully removed from the sample solution by washing with deionized distilled water. The sample solution is deaerated carefully with nitrogen gas for 10 minutes, followed by the addition of 1 mL of hexane, and is then acidified to approximately 6 M by adding deaerated concentrated hydrochloric acid. Immediately, the flask is stoppered. After 20-25 minutes, deaerated saturated sodium phosphate solution is added to the sample solution to partially neutralize the acidic sample solution. The electrode is immersed below the hexane layer, and the liberated iodine is titrated as described above. The endpoint is detected directly from the first-derivative titration curve. This titration volume corresponds to the concentration of chlorate ion (in equivalents).

The results for sub-mg/L level samples--after appropriate blank corrections --are shown in Table 8. It should be noted that better results are obtained by this modified single sample method. This is not surprising in that the concentrations of chlorite ion and chlorate ion are determined directly and continuously on the same sample, thus minimizing cumulative errors. This method is also applicable to determine individually the concentration of chlorite ion and chlorate ion in various mixtures at higher concentration levels with even better accuracy and precision (46).

Determination of Hypochlorite, Chlorite, and Chlorate Ions in Synthetic Mixtures.

For analyses of this type of mixture with several chlorine-containing oxidizing agents other than chlorate ion, the modified iodometric method and a modification of the Suzuki-Gordon method (6) were applied. The Suzuki-Gordon method is used to determine the chlorite ion concentration even in the presence of excess hypochlorite ion, which is of particular importance since drinking water treated with both chlorine dioxide and chlorine frequently has such a composition. On the basis of the same idea as that utilized for the determination of only chlorite ion and chlorate ion in a mixture, the modified iodometric method is used to determine directly the concentration of chlorate ion after the reduction of hypochlorite ion and chlorite ion by iodide ion at pH 2. The hypochlorite ion concentration is determined indirectly from the results obtained by the Suzuki-Gordon method and the modified iodometric method.

The sample solution is prepared in 60 mL glass-stoppered flasks by delivering known volumes of potassium chlorate solution, sodium chlorite solution, and sodium hypochlorite solution by using a Silverman syringe. Twenty mL of the borate buffer solution is added to the sample solution to adjust the pH to 10.5, followed by the addition of 0.001 g of sodium sulfite to reduce hypochlorite ion to chloride ion. After 1.5 minutes, the unreacted sulfite ion is oxidized to sulfate ion with excess 0.002 M iodine solution. In order to remove the excess iodine, the redox electrode is immersed in the sample solution and the sodium thiosulfate solution is added titrimetrically. The titration is stopped at the maximum point of the first-derivative titration curve obtained by the potentiometric method. After removal of the excess iodine, the sample solution is acidified to approximately pH 2 by adding the appropriate volume of 0.5 M hydrochloric acid in order to effect the reduction of chlorite ion to chloride ion. The liberated iodine is titrated with standard sodium thiosulfate solution. The endpoint is detected in the same manner as described above. This volume corresponds to the concentration of chlorite ion (in equivalents) and is symbolized as A.

Next, an identical sample solution is prepared. Immediately one mL of 0.015 M potassium iodide solution is added to the sample solution, followed by acidification to approximately pH 2 by the addition of an appropriate volume of 0.1 M hydrochloric acid. In this process, both the hypochlorite ion and chlorite ion are reduced to chloride ion. The iodine liberated is titrated by the same way as mentioned above. The titration is stopped at the maximum point of the first-derivative titration curve. This titration volume corresponds to the total concentration (in equivalents) of hypochlorite ion and chlorite ion, and is expressed as symbol B. After titration, the electrode is removed carefully from the sample solution by washing with deionized distilled water. The sample solution is deaerated with nitrogen gas for 10 minutes. Approximately 1 mL of hexane is added, followed by acidification to approximately 6 M by adding deaerated concentrated hydrochloric acid. Immediately the flask is stoppered. In this process, chlorate ion is reduced to chloride ion by iodide ion. After 20-25 minutes, deaerated saturated sodium phosphate solution is added to the sample solution to partially neutralize the acidity. The liberated iodine is titrated with standard sodium thiosulfate solution, and the endpoint is again detected potentiometrically. This titration volume corresponds to the concentration of chlorate ion (in equivalents) and is symbolized as C. The concentrations of hypochlorite ion, chlorite ion, and chlorate ion are calculated from (B - A), A, and C, respectively. The results are shown in Table 9. It is clear that the determination of hypochlorite ion, chlorite ion, and chlorate ion in mixture at the sub-mg/L level is possible by using the modified Suzuki-Gordon method and the modified iodometric method presented here.

The chemical reactions involved in the analysis described above are as follows:

$$SO_3^{2-} + ClO^- \rightarrow SO_4^{2-} + Cl^- \qquad \text{(pH 10.5)} \qquad (11)$$

$$SO_3^{2-} + I_2 + 2OH^- \rightarrow SO_4^{2-} + 2I^- + H_2O \qquad \text{(pH 9-10)} \qquad (12)$$

Table 9. Determination of Various Oxychlorine Species in Synthetic Mixtures

	Equiv/L HOCl x 10^{-6} N	Equiv/L ClO_2^- x 10^{-6} N	Equiv/L ClO_3^- x 10^{-6} N	Aggregate Oxid. Power
added	100.5	119.1	100.3	319.9
found	99.6	120.0	101.7	321.3
% error	0.9%	0.8%	0.4%	0.4%
added	8.741	9.613	9.957	28.311
found	8.60_1	9.81_4	9.78_6	28.20
% error	1.6%	2.1%	1.7%	0.4%

$$HClO + 2I^- + H^+ \rightarrow Cl^- + I_2 + H_2O \quad \text{(pH 2)} \qquad (13)$$

$$ClO_2^- + 4I^- + 4H^+ \rightarrow Cl^- + 2I_2 + 2H_2O \quad \text{(pH 2)} \qquad (14)$$

$$ClO_3^- + 6I^- + 6H^+ \rightarrow Cl^- + 3I_2 + 3H_2O \quad \text{(6 M } H^+\text{)} \qquad (15)$$

Furthermore, the disproportionation of iodine as shown in reaction (6)

$$3I_2 + 6OH^- \rightarrow IO_3^- + 5I^- + 3H_2O \qquad (16)$$

must be taken into account in that the method reported here iodine is added to the sample under basic conditions. By and large, it does appear that this potential difficulty can be avoided by using a large excess of iodide ion in the iodine solution as was originally suggested by Suzuki and Gordon (6).

Although the Suzuki-Gordon method is suggested for the determination of chlorite ion in the presence of hypochlorite ion (or hypochlorous acid) it is possible under some conditions to determine the combination by using the iodometric-potentiometric techniques at pH 7 followed by pH 2. However, this method cannot be used in the presence of high concentrations of hypochlorite ion since a portion of the iodine produced is further oxidized to iodate ion by the remaining hypochlorite ion.

This method has the distinct advantage that it is possible to determine the concentration of hypochlorite, chlorite, and chlorate ions even in mixtures containing relatively high hypochlorite ion concentrations--such as is frequently observed in a water treatment plant which is using both chlorine dioxide and chlorine. Furthermore, the present method can be used to determine directly the concentration of chlorite ion in contrast with the other indirect methods (11-13). Finally, measurements of synthetic mixtures containing hypochlorite, (actually at low pH values this corresponds to the combined free chlorine residual of hypochlorous acid plus chlorine) chlorite, and chlorate ions can be carried out with an accuracy of better than ±3% at the 0.3 mg/L level. Clearly this corresponds to a considerable improvement over existing methods.

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45. It should be noted that both normality (equivalents per liter) and mg/L are widely used in both the literature and in the field. In this context, mg/L is defined as [equiv/liter (as titrated) * 35.453 g/equiv * 1000 mg/L].

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APPENDIX A

CHLORATE ION AND THE AGGREGATE OF CHLORITE PLUS HYPOCHLORITE PLUS CHLORINE DIOXIDE

Method XXX.X (Titrimetric, Iodometric with Potentiometric Endpoint)

STORET NO.

1. Scope and Application

   1.1 This method is applicable to drinking water which has been disinfected with chlorine dioxide.

   1.2 The range of determination is 0.3 mg/L to 100 mg/L. The lower detection limit is 0.1 mg/L reported as free chlorine.

2. Definitions

   2.1 Chlorate ion, ClO_3^-, is an end product from disinfection by chlorine dioxide, or is an unreacted starting material from the generation of chlorine dioxide.

   2.2 Chlorite ion, ClO_2^-, is an end product from disinfection by chlorine dioxide, or is an unreacted starting material from the generation of chlorine dioxide.

   2.3 Hypochlorite ion, OCl^- (or hypochlorous acid, HOCl), is an unreacted starting material from the generation of chlorine dioxide.

   2.4 Chlorine dioxide is a disinfecting agent with the formula ClO_2.

3. Summary of Method

3.1 Chlorine dioxide, chlorite ion and free residual chlorine (chlorine, hypochlorite ion or hypochlorous acid) are simultaneously reduced to chloride ion with potassium iodide at pH 2. The iodine which is stoichiometrically liberated is titrated with sodium thiosulfate to a potentiometric endpoint. The concentration of chlorine dioxide plus chlorite ion plus hypochlorite ion or hypochlorous acid is calculated as mg/L of chlorine.

3.2 In the same solution chlorate ion is then reduced to chloride ion with potassium iodide in 6 M hydrochloric acid under a layer of hexane followed by neutralization with saturated sodium phosphate solution. The iodine which is liberated is titrated with sodium thiosulfate to a potentiometric endpoint. The concentration of chlorate ion is calculated as mg/L of chlorine.

3.3 The sum of calculated concentrations is the total oxidant as chlorine for drinking waters treated with chlorine dioxide.

4. Interferences

4.1 All other oxidizing agents interfere but are usually present in insignificant concentrations in drinking water.

5. Sample Handling and Preservation

5.1 Chlorine species are extremely unstable and cannot be stored. Determinations must be started immediately after sampling. Avoid excess light and agitation.

6. Apparatus

6.1 Silverman syringes:[11.3] The volume of the syringe is calibrated by weighing distilled water at constant temperature (accuracy and precision ±3/10,000 or better).

6.2 Combination redox electrode: The details of the electrode are shown in Figure A-1.

6.3 Metrohm Herisau Model E 535 auto buret: Used for the standard sodium thiosulfate titrations.

6.4 Metrohm Herisau Model E 536 potentiometer: Used for detection of the titration end point.

7. Reagents

7.1 Sodium Thiosulfate, Stock Solution (0.2 N): Dissolve 24.82 g $Na_2S_2O_3 \cdot 5H_2O$ in boiled and cooled distilled water and dilute to 1 liter. Preserve by adding 5 mL chloroform.

7.2 Sodium Thiosulfate Titrant (0.0005 N): Dilute 5.0 mL of stock solution (7.1) to 1.0 liter. Preserve by adding 5 µL of chloroform. Prepare fresh daily. Standardize with 0.005 N potassium biiodate (7.3, 7.12).

7.3 Potassium Biiodate Standard (0.0005 N): Dissolve 3.567 g of potassium biiodate, previously dried 2 hours at 103°C, in distilled water and dilute to 1.0 liter. Dilute 5 mL to 1 liter for 0.0005 N biiodate solution.

7.4 Potassium iodide solution (0.015 M): Dissolve 0.25 g of potassium iodide in 100 mL deionized distilled water. Store in a brown glass-stoppered bottle.

7.5 Nitrogen gas (Reagent grade): The nitrogen gas used for deaeration is passed through a scrubber containing 0.1 M chromium(II) in 1 M sulfuric acid (7.18) to remove traces of oxygen.

7.6 Concentrated hydrochloric acid (Reagent Grade): The concentrated acid is deaerated by purging with nitrogen gas (7.5).

7.7 Hydrochloric acid solution (0.1 M): This is prepared by diluting one part of the concentrated hydrochloric acid with 120 parts distilled water.

7.8 Hexane: Spectroanalyzed grade hexane is used without further purification.

7.9 Saturated sodium phosphate solution (Na_2HPO_4): A saturated solution of $Na_2HPO_4 \cdot 12H_2O$ is prepared using hot deionized distilled water. The cooled solution is deaerated with nitrogen gas (7.5).

7.10 Potassium Iodide (KI): Crystals, ACS Reagent Grade.

7.11 Sulfuric Acid Solution (1:4): Slowly add 200 mL H_2SO_4 (Sp. gr. 1.84) to 800 mL of distilled water.

7.12 Standardization of 0.0005 N Sodium Thiosulfate: Dissolve approximately 2 g (±0.1 g) KI (7.10) in 100 to 150 mL distilled water; add 10 mL H_2SO_4 solution (7.11) followed by 20 mL standard 0.0005 N potassium biiodate solution (7.3). Place in dark for 5 minutes, dilute to 300 mL and titrate with the 0.0005 N sodium thiosulfate (7.2) to the potentiometric endpoint as described in 8.5, 8.6, and 8.7. Run in duplicate.

7.13 Zinc, mossy, reagent grade.

7.14 Chromium(III) sulfate$\cdot XH_2O$, reagent grade.

7.15 Mercury(II) chloride, reagent grade.

7.16 Amalgamated zinc: Wash mossy zinc (7.13) with a saturated solution of mercury(II) chloride (7.15), rinse with distilled water and 0.1 M sulfuric acid.

7.17 Chromium(III) sulfate solution (approximately 0.1 M): Dissolve approximately 35 g of chromium(III) sulfate·XH_2O (7.14) in 1.0 M sulfuric acid in a one liter flask. Dilute to the mark with 1.0 M sulfuric acid.

7.18 Preparation of Deoxygenation Scrubber: Place amalgamated zinc (7.16) in a 250 mL fritted glass scrubbing tower to the height of 2-3 centimeters. Add chromium(III) sulfate solution (7.17) to cover the amalgamated zinc (7.16) by 4-5 centimeters. Flush with nitrogen and seal from the atmosphere using tubing and clamps. When the solution changes from a dark green-purple to light sky blue color the tower is ready to deoxygenate the nitrogen gas (7.5).

8. Procedure

8.1 Deliver 5.0 mL of sample solution (or an appropriate sample containing 5×10^{-5} meq potassium chlorate) to a 60 mL glass-stoppered flask by using a Silverman syringe (6.1).

8.2 Add 1 mL of 0.015 M potassium iodide solution (7.4). Mix thoroughly.

8.3 Add 2 mL of 0.1 M hydrochloric acid (7.7) to allow the iodide ion to reduce chlorine dioxide, chlorite ion and hypochlorite ion (or hypochlorous acid) to chloride ion.

8.4 Allow the sample to stand for 5 minutes in the dark.

8.5 Immerse the electrode (6.2) in the sample solution.

8.6 Titrate the liberated iodine with standard sodium thiosulfate solution (7.2) at the speed of 0.05 mL/min by using the autoburet (6.3).

8.7 Stop the titration at the maximum point of the first-derivative titration curve obtained by the potentiometer (6.4). This titration volume corresponds to the total concentration of chlorine dioxide, chlorite ion and hypochlorite ion (or hypochlorous acid).

8.8 Remove the electrode from the sample with careful washing of the electrode with deionized distilled water.

8.9 Deaerate with nitrogen gas (7.5) for 10 minutes.

8.10 Add 1 mL hexane.

8.11 Add 15 mL of deaerated concentrated hydrochloric acid (7.6), and stopper the flask immediately.

8.12 Allow the sample solution to stand for 25 minutes in the dark.

8.13 Add 15 mL of deaerated saturated sodium phosphate solution (7.9). Mix.

8.14 Immerse the electrode (6.2) under the hexane layer.

8.15 Titrate the liberated iodine with standard sodium thiosulfate solution (7.2) at the speed of 0.05 mL/min by using the auto-buret (6.3).

8.16 Detect the endpoint from the first-derivative curve obtained potentiometrically (6.4). The titration volume corresponds to the concentration of chlorate ion.

8.17 Measure the blank titration volume by using the same procedures described in 8.1 thru 8.16 except for using deionized distilled water instead of the drinking water sample.

8.18 Calculate the actual concentrations of total chlorine dioxide, chlorite ion and hypochlorite ion (or hypochlorous acid), and chlorate ion from the titration volumes obtained after subtracting the blank titration volumes obtained in 8.17 from the titration volumes obtained in 8.7 and 8.16, respectively.

9. Calculations

9.1 The concentration in mg/L of available chlorine is calculated directly from the titration volume (8.18).

$$(\text{equiv/liter})_{\text{meas.}} = (\text{corrected titration volume in mL})(N\ S_2O_3^{=})$$

$$\text{mg/L} = (\text{equiv/liter})_{\text{meas.}}(35.459\text{g/equiv})(1000\ \text{mg/gm})$$

10. Precision and Accuracy

The precision and accuracy have not yet been precisely determined. Preliminary experiments indicate an accuracy of 5/1000 over the entire concentration range and a precision of 3/1000.

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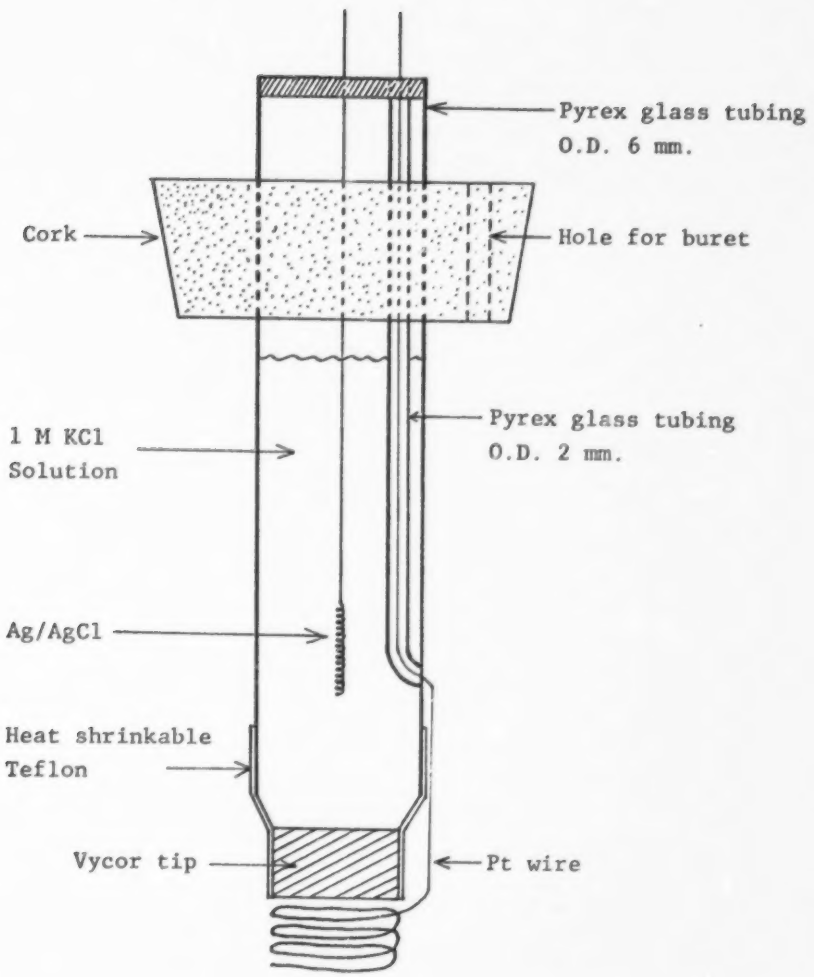

Figure A-1. Combination redox electrode